11. A New Pentamethine-cyanine Synthesis caused by the Decomposition of an Acid Anhydride.

By Tuneyuki KIMURA.
Research Laboratory of Fuji Film Company.
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In the previous communication it was reported by the present author that the formation of cyanines proceeded smoothly when mixed solvents were applied, while the utilization of the single solvent-pyridine or acetic acid anhydride alone provoked poorer yields of cyanines.

Here will be reported the new synthetical method of pentamethine-cyanines by the analogous application of the mixed reagents-pyridine and acetic acid anhydride upon an arylamino-ethenyl-cycloammonium salt which had been briefly referred to in the preceding paper. It must especially be emphasized that the acetic anhydride plays an important rôle as regard to the cyanine-synthesis as well as the malonic acid.

The following cyanine-dyes were synthesized by this new method with tolerable yields: 1,1'-diethyl-2,2'-benzothia-pentamethine cyanine, 1,1'-diethyl-2,2'-benzoselena-pentamethine cyanine and their substitution products amounting to more than 40% yields, while 1,1'-diethyl-2,2'-benzoxa-pentamethine cyanine was obtained with about 20% crop. Here must be urgently noticed that the latter had never been attained by the propendianil method.

This new process will perhaps proceed following: at first arylamino-ethenyl-cycloammonium salt is acetylated through acetic anhydride while the latter facilitates the splitting off of acetanilide from the resulting acetoarylaminio-ethenyl-cycloammonium salt. Two parts of the remaining ethenyls will be connected with a methine which is afforded by the decomposition of acetic anhydride.

Thus pentamethine cyaninine will be formed.

T. Ogata synthesized pentamethine cyanines with applying triethylamine and malonic acid upon acetarylamino-ethenyl-cycloammonium salt.\textsuperscript{13}

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\begin{align*}
2(C_nH_{2n+1})-CH=CH-N & \xrightarrow{R X} COCH_3 COOH \\
\rightarrow (C_nH_{2n+1})-CH=CH-CH=CH-(C_nH_{2n+1}) & + 2(NHCOCH_3 + 2CO_2)
\end{align*}
\]

Under the circumstances behaved the malonic acid as the supplier of methine group in the formation of cyanine-colour. The present author employed this time acetic acid anhydride with success in place of malonic acid as the methine supplier. In order to prove that the acetic anhydride furnishes the methine group in my cyanine formation, the present author applied pyridine and an acid anhydride of a higher homologue of acetic acid. In this case the meso-alkyl-pentamethine cyanine was obtained which was identical with regard to the photographic, analytical and other physical properties with that of the Ogata’s one who had applied alkyl-malonic acid as the methine supplier in his corresponding cyanine synthesis.

For example, 1,1’-diethyl-9-methyl-2,2’-benzothia-pentamethine cyanine (sensitizing maximum 690 \( \mu \mu \), decomposition point 273\( ^\circ \) C), and 1,1’-diethyl-9-methyl-2,2’-benzoselena-pentamethine cyanine (sensitizing maximum 720 \( \mu \mu \), decomposition point 234\( ^\circ \) C) were obtained by means of procedure with the average yield of 25%.